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Original Research Article

Granular Activated Carbon (GAC) Adsorption of Herbicide (Metsulfuron methyl) in Water and Doping Zn-TiO₂ Activated Carbon Coupling with Batch Photocatalytic Oxidation

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ABSTRACT

The granular activated carbon (GAC) filter was found to be very effective as a treatment for the removal of herbicide. The Sips isotherms showed the best fit with 6.6% error. Fixed bed column experiments packed with GAC were conducted with different GAC bed heights (5, 10 and 15 cm) and different effluent velocities. The GAC fixed bed column show the model simulation fits reasonably well during the initial period and also with a shallow bed depth (5 cm) with flow rate 4 m/h. Another set of experiment is GAC and GAC doping Zn with various concentrations to remove herbicide from water. The doped Zn – Tio_2 GAC batch experiments can remove MM in term of DOC from 60 to 77% by using different w/v of doped Zn onto TiO_2 – GAC. The highest remove of MM 77% by using batch experiment was 0.125% w/v Zn -TiO_2.

KEYWORDS

Herbicide, Granular activated carbon, Adsorption, Sips, Fixed bed, Doped Zn-GAC.

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INTRODUCTION

The use of activated carbon such as granular activated carbon filter, to remove synthetic organic compounds (SOCs) and organic pollutants from water are known as a highly efficient but simple technique. GAC adsorption is used when the removal of organic compounds is necessary on a continuous basis and when long contact times are needed for effective removal [1]. The effects of these modifications on the adsorption properties of activated carbons against herbicides in this case metsulfuron methyl (MM) in aqueous solution was analyzed. The idea was to explain the mechanism of the adsorption process. The several studies used in research were aqueous solutions of individual herbicides for one pH value and one (room) temperature [2-5]. The most Langmuir and Freundlich isotherms equations were used for the mathematical description of adsorption equilibria. Some of the works also used Sips. The kinetics of the adsorption process, pseudo-first-order (PFO) and pseudo-second-order (PSO) models were most often used. For the various pH, adsorption equilibrium capacities of the phenoxy herbicides increased with a decrease in pH of the solution. The adsorption characteristics of phenoxy herbicides from an aqueous solution on the active carbon materials (GAC, F-400) were studied and the Sips equation were used for adsorption equilibrium isotherms [6]. Another study by discussed in details using Sips equation was described, Single-component of herbicides (2,4-D (2,4-dichlorophenoxy acetic acid) and 2,4-DNP (2,4-Dinitrophenylhydrazine) have been measured for adsorption equilibria. The herbicides were dissolved in water and three kinds of GACs (F400, SLS103, and WWL). To simulate isothermal adsorption behavior in a fixed bed adsorber, the linear driving force approximation (LDFA) model was used and successfully simulated experimental adsorption under various operation conditions [7]. In this study, a single component of herbicides (Metsulfuron methyl) was used in batch and fixed bed adsorption. The GAC was used for adsorption equilibria and for fix bed GAC.

EXPERIMENTAL SET UP AND DESCRIPTION

Fourth groups of experiments were conducted. The first set was conducted with granular activated carbon (GAC). The purpose of these experiments was to investigate the single component equilibrium adsorption of GAC. Adsorption equilibrium experiments were conducted by adding different amount of GAC ranging from 0.15–2.75 g/L into a 250 mL flask containing 100 mL of metsulfuron methyl at a concentration of 10 mg/L. All flasks were shaken continuously at room temperature (25°C) for 72 hours on a shaking table at speed 130 rpm. After 72 hours of shaking, sample were taken from all flasks and filtered through a 0.45 µm filter prior to TOC analysis. The adsorption of GAC was determined using the following equation

$$q = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

where C_0 is the initial TOC concentration of metsulfuron methyl (mg/L), C_e is the final concentration of metsulfuron methyl (mg/L), V is the volume of the solution (mL), and M is the weight of GAC (g).

The second set of experiment used GAC in a fixed bed columns. These experiments were conducted using transparent acrylic filter columns with dimensions of 2 cm in diameter and 150 cm in length. The column had outlet pipes along its length and at the bottom of the column. The GAC was packed into the column up to the required depth. The columns were operated in a downflow mode. Feed water was pumped from a water tank to the top of the columns and passed through the filter bed. An overflow outlet was placed above filter bed to maintain a constant head above the GAC filter bed. Effluent samples were collected from the bottom of the column for analysis. One series of experiments were conducted with different flow rates of 1 M/h, 2 M/h and 3 M/h with a fixed 5 cm GAC bed depth. Another series of experiments used different bed depths of 5 cm, 10 cm, and 15 cm with a fixed flow rate of 4 M/h. The experimental set up is shown in Figure 1.

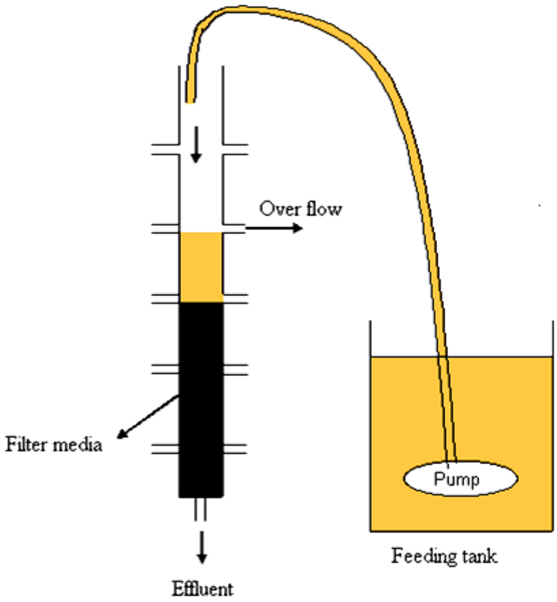

Figure 1. Schematic of GAC column

Another set of experiment is doping Zn - GAC and use batch experiment to test efficiency of adsorption. This experiment use AR chemical grades which are ethyltrimethyl ammonium bromide (MW 364.45 g/mol) SRL Co., Ltd., titanium (IV) isopropoxide (MW 284.22 g/mol) Sigma Aldrich, Co., Ltd., acetylacetone (MW 100.12 g/mol) Sigma Aldrich, Co., Ltd., . ethanol 99.9% RLC Labscan, Co., Ltd., and zinc Powder (MW 65.38 g/mol), Kemaus, Co., Ltd.. The furnace using in this experiment is GALLENKAMP Muffle furnace size 3. The experimental procedure started from coating the activated carbon surface with zinc oxide/titanium dioxide (ZnO/TiO_2) particles to obtain functional activated carbon (FAC) by sol–gel process using zinc sulfate ($ZnSO_4$) and titanium (IV) isopropoxide as precursors. Firstly, zinc sulfate ($ZnSO_4$) solution was prepared by weighing 0.01 g of $ZnSO_4$ powder and dissolving it in 80 ml of deionized water. $ZnSO_4$ solution concentrations were prepared by weighting $ZnSO_4$ powder 0.025, 0.1, and 0.125, respectively. Secondly, a mixture of titanium(IV) isopropoxide and acetylacetone was prepared at a molar ratio of 1:1 and weigh 10 g of acetylacetone and add titanium(IV) isopropoxide to obtain a molar ratio of 1:1. Mix the substances prepared from steps 1 and 2, add 20 ml of ethanol each, and stir the mixture with a magnetic stirrer for 4 hours to obtain the activated carbon coating substance. Weighting granular activated carbon and immerse in an ultrasonic bath for 1 hour. Activated carbon is immersed in the coating solution in the ultrasonic bath and separate coating solution and coating activated carbon by centrifuge as shown in Figure 2. The coating activated carbon are dried in an oven to remove moisture. The separated clear part is centrifuged and moister is removed by oven. Finally, coating activated carbon dried at 500°C for 1 hour.

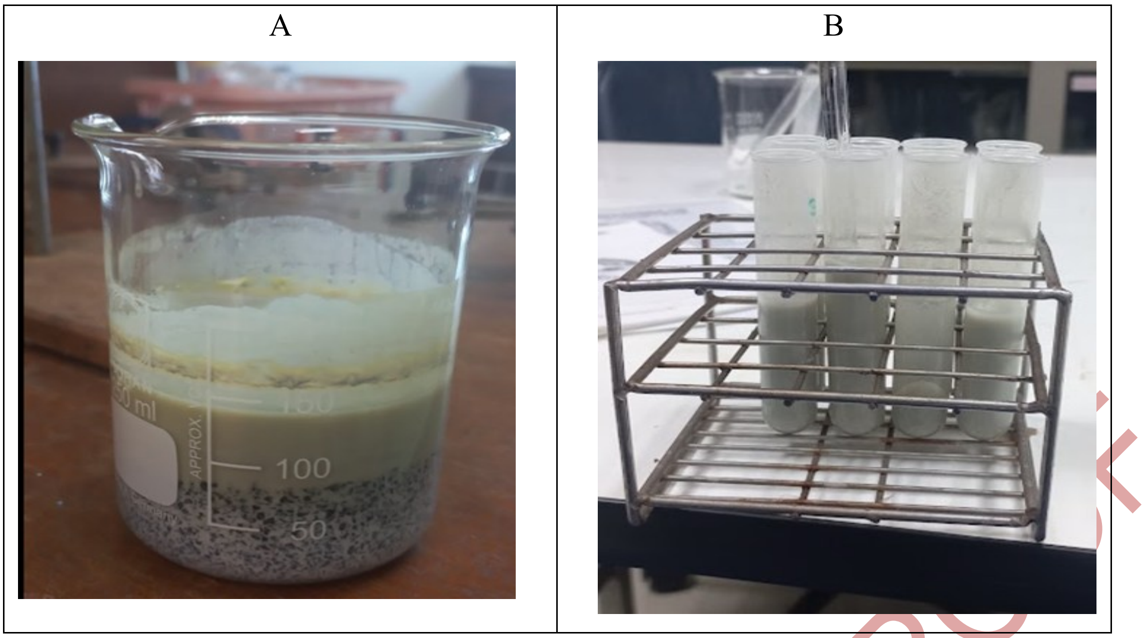

Figure 2. A. Sonicated doping $ZnSO_4$-TiO_2 GAC in solution 2B. separated solution

The study of doping GAC with ZnO_4- TiO_2 (Figure 3.) surface after dried at 500°C by using scanning electron microscope is shown in Figure 4.

Figure 3. Dried Zn doped– TiO_2 GAC after dried at 500°C

- Scanning Electron Microscope, SEM, JEOL, JSM 5410LV, Japan, and operated at 200 kV. From the SEM test, it can be observed that the synthetic doped Zn - TiO_2 GAC has different crystal characteristics. This can be observed from the small particles in the nano level at the surface of the GAC, whereas the GAC does not have small particles (Figure 4 A, B, C) in the nano level at the surface of GAC. Agglomerated Zn onTiO_2 are not in the different shaped morphology (figure 4 C) at the 40000x of SEM ETD detector simple size of GAC. In the small size of GAC (Figure 4 D), the similar shaped morphology of doped Zn – TiO_2 on GAC occurred as shown in Figure 4 F at the 40000x of SEM ETD detector.

The SEM analysis was used for morphological studies. The SEM images showed the agglomerate shaped nanomaterials with the varied size 30 µm size range.

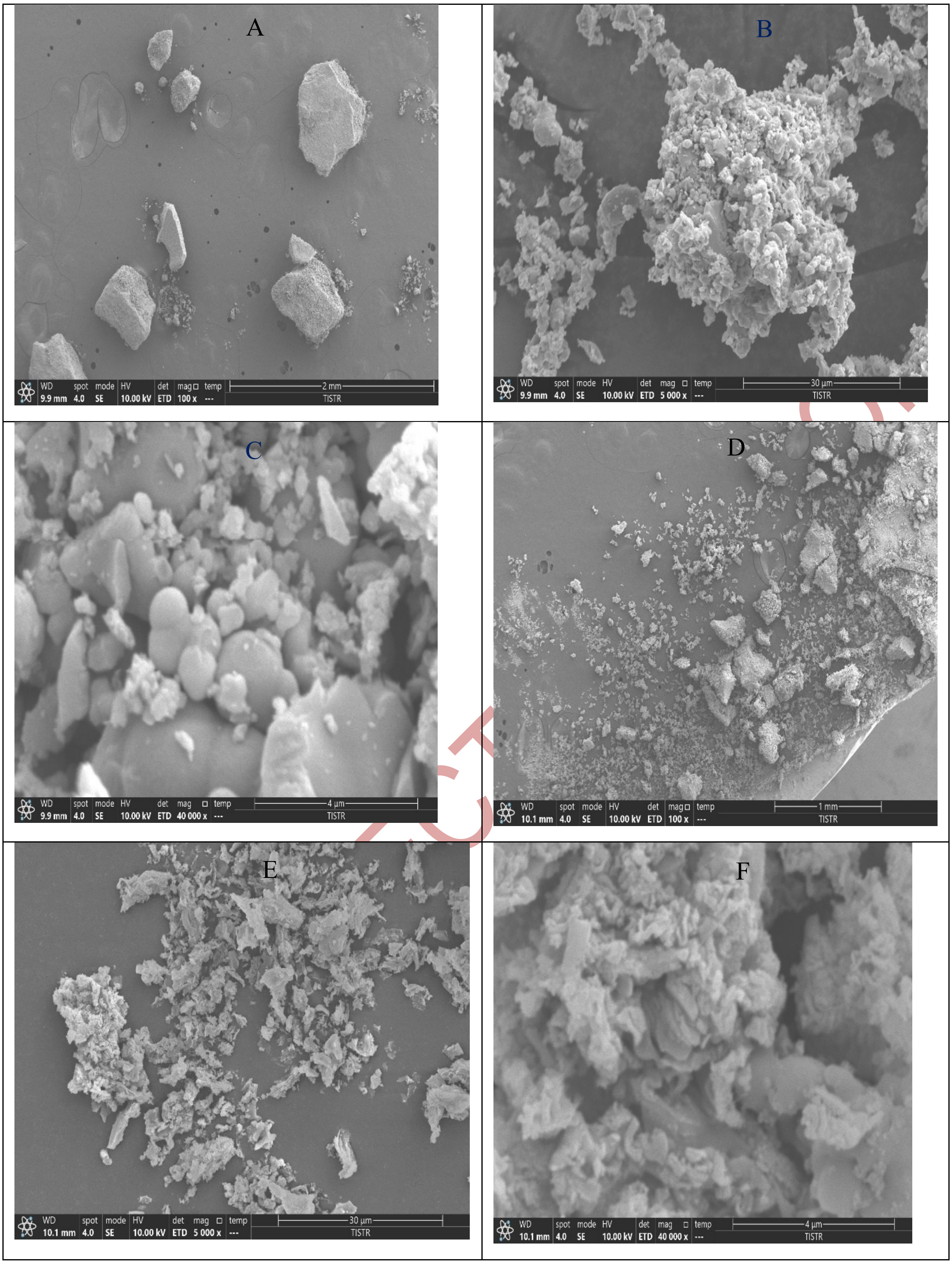

Figure 4 (A – E). Scanning electron microscope of Zn doped TiO_2 - GAC mode SE, detector ETD with different magnify (4A) 100x of doped GAC (4B) 5000x of doped GAC (4C) 40000x of doped GAC (4D) small pellet of doped GAC 100x (4E) small pellet of doped GAC 5000x (4F) small pellet of doped GAC 10000x

The third experiment set up is batch adsorption for GAC and doped - GAC experiment with bath/ magnetic stirrer brand PMC model 500 P-2 230 V 0.1 AMP 50 W, to test doped GAC. The 1000 mL beaker contain 10 mg/L metsulfuron methyl (MM) solution at temperature control 25°C with tap water in water bath and use 120 rpm of magnetic stirrer to uniform mixing for 1 hr. The sample was take out from the pump with control valve to test DOC.

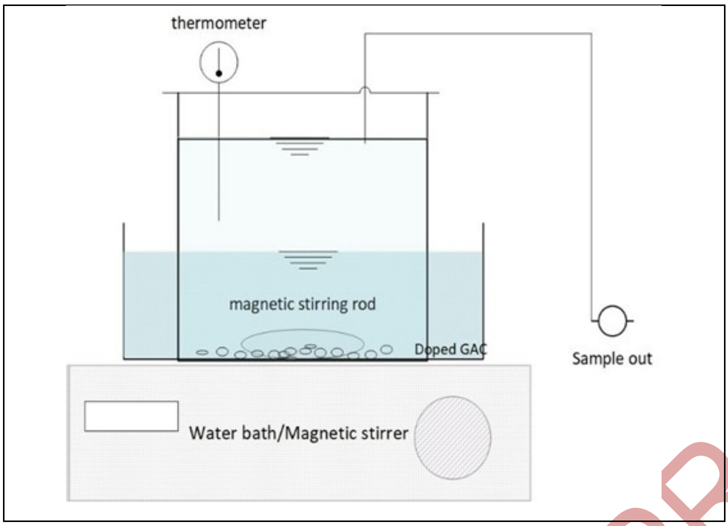

Figure 5. Batch adsorption processes with 25°C control by tap water in water batch and 120 rpm

The last experiment is batch photocatalytic oxidation with UVC submersible UV lamp SOBO T5- UV 5 W with the same condition of batch adsorption processes. However, the 1000 mL beaker was cover with foil to protect irradiate and irritate of UVC as shown in Figure 6.

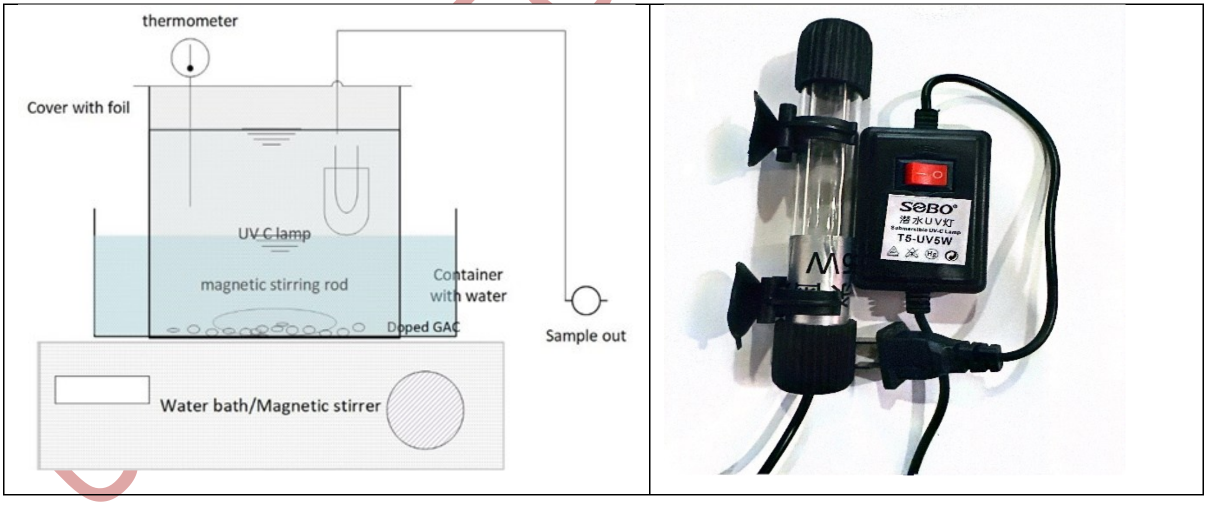

Figure 6. Batch photocatalytic oxidation with 5 watts UVC 254 nm. 120 rpm and 25°C

Adsorption equilibrium

A satisfactory description of the equilibrium state between two phases (solid and liquid)) is important for a successful representation of the dynamic behaviour of the adsorption system. Various isotherm models were used including the Langmuir and the Freundlich models which are the most common isotherm models that describe the equilibrium between the two phases (solid and liquid). These isotherm models are widely accepted because of their simplicity. In addition to these models, A Sip model was also used in the analysis.

Langmuir isotherm

The development of a Langmuir model is based on the following assumptions [8];

- adsorption happens in definite localised surface sites;
- each site binds with only one molecule;
- all identical sorption sites in adsorbent surfaces are energetically uniform and homogeneous: and;
- no interaction occurs among adsorbed molecules.

The Langmuir isotherm is described as

$$q = \frac{aC}{1 + bC} \tag{2}$$

where,
q = amount adsorbed (mg/g)
a, b = isotherm constants
C_e = equilibrium concentration of metsulfuron methyl

The reciprocal of Equation 2 gives,

$$\frac{1}{q} = \frac{1}{ab} + \frac{1}{bC_e} \tag{3}$$

Equation 3 gives a straight line when 1/C is plotted against 1/q with 1/a as an intercept and 1/b as gradient.

Freundlich isotherm

The Freundlich isotherm describes heterogeneous surface adsorption. It differs from Langmuir isotherm and the energy distribution for adsorptive sites follows an exponential type function which is close to the real situation. Therefore, the rate of adsorption/desorption varies with the strength of the energy at the adsorptive site. The Freundlich isotherm is more accurate than the Langmuir isotherm but it does not satisfy Henry's law at low surface coverage [9]. The Freundlich isotherm is usually expressed by Equation 4 with the following assumptions;

- no association or dissociation of molecules occur after they are adsorbed on surface ;
- there is a complete absence of chemisorption ;

$$q = KC_e^{1/n} \tag{4}$$

where,
q = amounted adsorption (mg/g)
C_e = equilibrium concentration of metsulfuron methyl (mg/L)
K_F = Freundrich isotherm constant (mg/g)
n = Freundrich isotherm constant dimensionless

The logarithm of Equation 4 gives,

$$\text{Log } q = \log K + (1/n) \log C_e \qquad (5)$$

when log q is plotted against log C_e, log K is the intercept and 1/n as gradient. The following figure shows the companion of the Langmuir and Freundlich isotherm for a system pattern of adsorption of fluoxetine HCl (Prozac) from simulated gastric fluid to Norit USP powdered activated carbon (Figure 1). It can be seen that the Freundlich isotherm has a much sharper rise at low C_e values (caused by the high energy sites, which bind well even at low Ce). Normally, the Freundlich equation tends to fit data on adsorption from liquid solutions better, while the Langmuir equation sometimes fits data on adsorption of gases to solids a bit better [8]. The Sips isotherm is a model that can be viewed as a combination of both the Langmuir and Freundlich models. The equilibrium curve obtained from the Sips model is similar to the Freundlich model if the initial solute concentration is low, while at higher solute concentrations the Sips model follows the Langmuir model. The Sips isotherm model is expressed by Equation 6.

$$q = \frac{qmC^{\frac{1}{n}}}{1 + K_s C^{\frac{1}{n}}} \qquad (6)$$

where,
C is equilibrium organic concentration (mg/L)
q_m is saturation amount of organic adsorbed (mg/g)
K_S is the Monod half velocity coefficient

Adsorption equilibrium experiment of GAC was conducted using a constant concentration of Metsulfuron methyl of 10 mg/L. The purpose of this study was to find the single component equilibrium concentration of herbicide. The adsorption behavior was simulated using the Langmuir, Freundlich, and Sips isotherm. Adsorption parameters and the coefficients of Equation 2, 4, and 6 are shown in Table 1.

Table 1. Equilibrium adsorption isotherm parameters

Isotherm models					
Langmuir		**Sips**		**Freundlich**	
Parameter	Value	Parameter	Value	Parameter	Value
qm	1.26	qm	1.975		
b	0.80	b	0.185	k	0.32
		n	0.255	n	0.45
%Error	15.72	%Error	6.60	%Error	7.07

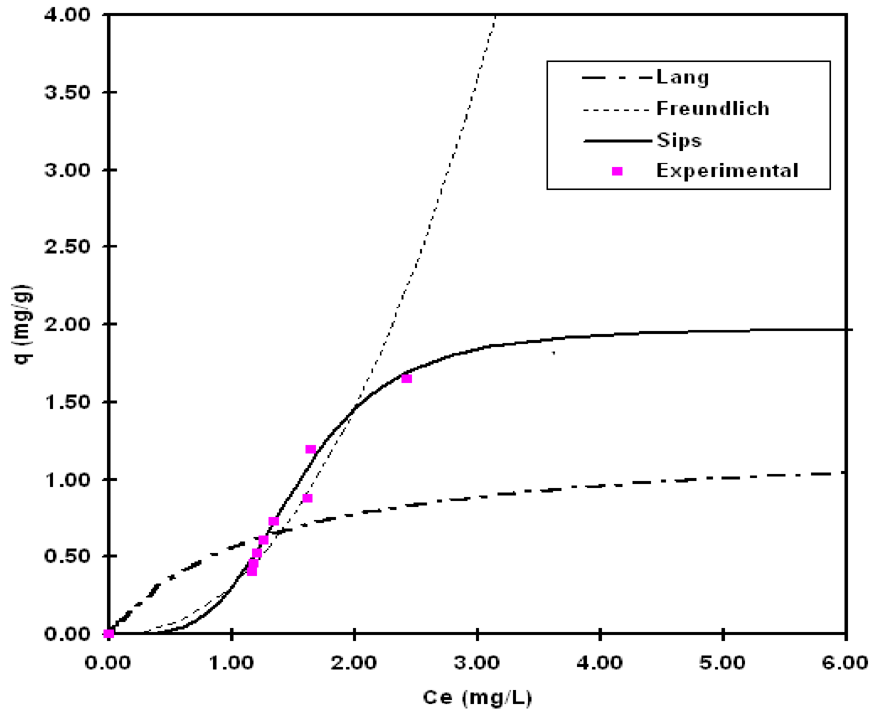

Figure 7. Adsorption equilibrium of metsulfuron methyl by GAC with different isotherm models (contact time = 72 hours, mixing rate 130 rpm, temperature 25°C)

In this study, the results shown in Figure 7. indicate that the Sips isotherm describe the GAC equilibrium adsorption reasonably well. The average error between experimental and simulated values was calculated using the following equation:

$$\text{Error}\% = \frac{100}{n}\sum_{I=1}^{n}\left[\frac{q_{\text{exp.n}} - q_{\text{cal.n}}}{q_{\text{exp.n}}}\right] \qquad (7)$$

where $q_{\text{exp.n}}$ and $q_{\text{cal.n}}$ were respectively, the experimental and calculated values of the amount of adsorption and n denotes the number of samples.

The Sips isotherm fitted the experimental data reasonably well with an error of 6.6 % compared with 15.72 % and 7.07% for the Langmuir isotherm and Freundrich isotherm respectively. Furthermore, the shape of the curve describing the experimental data shows that with a high concentration of GAC the isotherm is closer to with the Freundrich isotherm. In contrast, at low concentrations of GAC, the trend of the experimental data favours the Langmuir isotherm [10]. Overall the Sips isotherm gave the best fit with the experimental data because it is essentially a combination of both Freundrich and the Langmuir models [11].

Effect of Filtration Rate in GAC column

Columns with a 5 cm GAC bed depth were operated at filtration rates of 1, 2 and 4 m/h to study the effect of the filtration rate on TOC removal efficiency (Figure 8.).

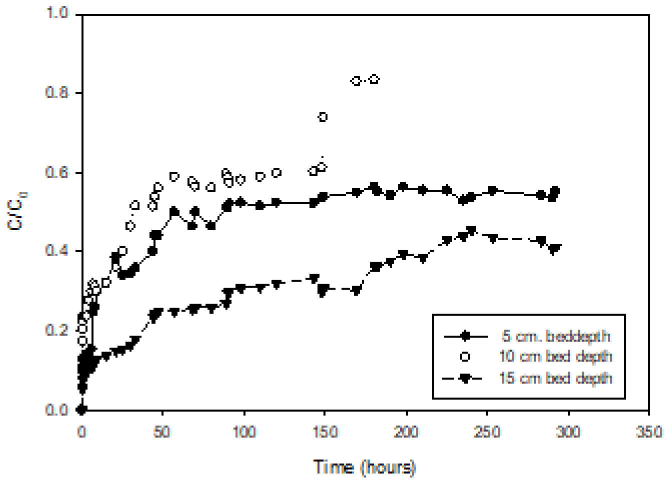

Figure 8. Influence of filtration rate on the performance of adsorption of a 5, 10, 15 cm deep GAC bed. Average influent DOC = 10 mg /L

The efficiency of herbicide removal decreased with the filtration rate increase. For a GAC filter of 5 cm bed depth and 15 cm bed depth the DOC removal increased from less than 30% to 60% when filtration rate decreased from 4 to 1 m/h [12]. The empty bed contact time (EBCT) decreases when the velocity increases in a similar way as Chaudhary *et al.* (2003) in the study with biologically treated sewage effluent (BTSE) [13] claimed that DOC removal increased from 29 to 51.2% with an increase EBCT from 5 to 20 minutes [13-15]. For small GAC bed depths of 15 cm, the difference is more clearly apparent when comparing the results at a filtration rate of 4 m/h with 1 m/h but less obvious between filtration rates of 1 m/h and 2 m/h.

Fixed Bed Adsorption Mathematical Model

A mathematical model was developed to simulate the removal efficiency of the GAC fixed bed adsorption system. The model is principally based on the transport by advection and diffusion processes and adsorption on GAC particles. The adsorbent particles are assumed to be spherical in shape and uniform in size while the curvature effect of the adsorbent surface was ignored. No biological reaction was assumed to occur. The mass balance equations and the boundary conditions of the fixed bed adsorption system in dynamic conditions are given by the following equations and were previously discussed by Chaudhary *et al.* (2003) [13].

$$\frac{\partial C}{\partial t} = D_{ax}\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - \frac{\partial C}{\partial z} - \frac{(1-\varepsilon_b)}{\varepsilon_b}\frac{3k_f}{R}(C - C_{pi}) \qquad (8)$$

where:
The initial and boundary conditions are:-
C = concentration in bulk solution, mg/L
C_{pi} = concentration inside particle, mg/L
D_{ax} = axial dispersion coefficients, m^2/s
k_f = external film mass transfer coefficient of organic, m/s
R = radius of adsorbent particle, m
u = velocity of the fluid, m/s
z = bed depth, m
ε_b = bed porosity

The initial and boundary conditions are:-
Initial condition, C = 0
Boundary condition,
at z=0 is $D_{ax}\frac{dC}{dz} = -v(C\big|_{z=0^-} - C\big|_{z=0^+})$

and at z=L is $\frac{dC}{dz} = 0$

The mass transfer rate was described by linear driving force approximation (LDFA) model. It was selected because of its simplicity and use of a lumped parameter such as TOC to represent the liquid phase concentration of the system. It is assumed in the model that the rate of adsorption to a particle is linearly proportional to a driving force developed from the difference between the concentration at the surface of the particle and the average adsorbed-phase concentration within the particle.

The overall mass balance is given by the following equation.

$$V.\frac{dC}{dt} + M.\frac{dq}{dt} = 0 \qquad (9)$$

The mass transfer equation of the model is given by

$$\frac{dq}{dt} = k_s.(q_s - q) \qquad (10)$$

where:
V = volume of the solution in batch reactor, L
M = weight of the adsorbent, g
q = Average adsorbed phase organic concentration, mg/g
q_s = Adsorbed phase concentration at the external surface of adsorbent particle, mg/g
k_s = particle phase mass transfer coefficient, s^{-1}

Several isotherms are available in the literature [16]. Figure 2. shows the Sips adsorption isotherm was successful in describing the overall adsorption isotherm of MM. Therefore, in this study, the Sips equation (equation 11) was used to simulate the adsorption process.

$$q_s = \frac{q_m.b.C^{1/n}}{1 + b.C^{1/n}} \qquad (11)$$

where q_m is the maximum adsorption capacity of adsorbent, and b and n are the constants in isotherm equation.

The coupled parabolic second-order partial differential equations, equations 8 to 11, cannot be solved analytically. Therefore, the preferred means of numerically solving this set of partial difference equations is by the explicit finite difference method using the prescribed boundary conditions.

Table 2 Parameters used for model simulation of GAC filter

Parameter	Value				
Bed depth (cm)	5	5	5	10	15
Velocity (M/hr)	1	2	4		
TOC of influent (mg/L)	10				
Particle phase mass transfer coefficient, k_s, (x10^{-5}) (s^{-1})	16		4		
External film mass transfer coefficient k_f (x10^{-5}) (m/s)	1.5	1.75	1.2*	1.2	
Axial dispersion coefficient D_{ax} (x10^{-5}) (m^2/s)	1				

* values of k_f used in Figure 4.

Table 6.2 presents the estimated values of the parameters that were used in modelling the GAC filter. The axial dispersion coefficient, D_{ax} was based on values suggested by Chaudhary *et al.* (2003) [13]. D_{ax} was kept constant while the filter bed depth, TOC influent concentration and filtration rate were set to match the experimental conditions, (see Table 2). The mass transfer coefficients, k_f and k_s were obtained by fitting simulated model values to the experimental data. k_f and k_s were kept constant for modelling the effect of bed depth (see Figure 4) as it is not believed that these parameters should not vary significantly for this situation [13]. k_f and k_s was varied for modelling the effect of filtration rate as these parameters are dependent on the fluid velocity and particle diameter [13]. For this case, kf was 1-1.75E^{-5} and k_s was 1.6E^{-4} for both the v = 1 and 2 M/hr and k_s was 4E^{-5} for v = 4 M/hr (see Figure 9.).

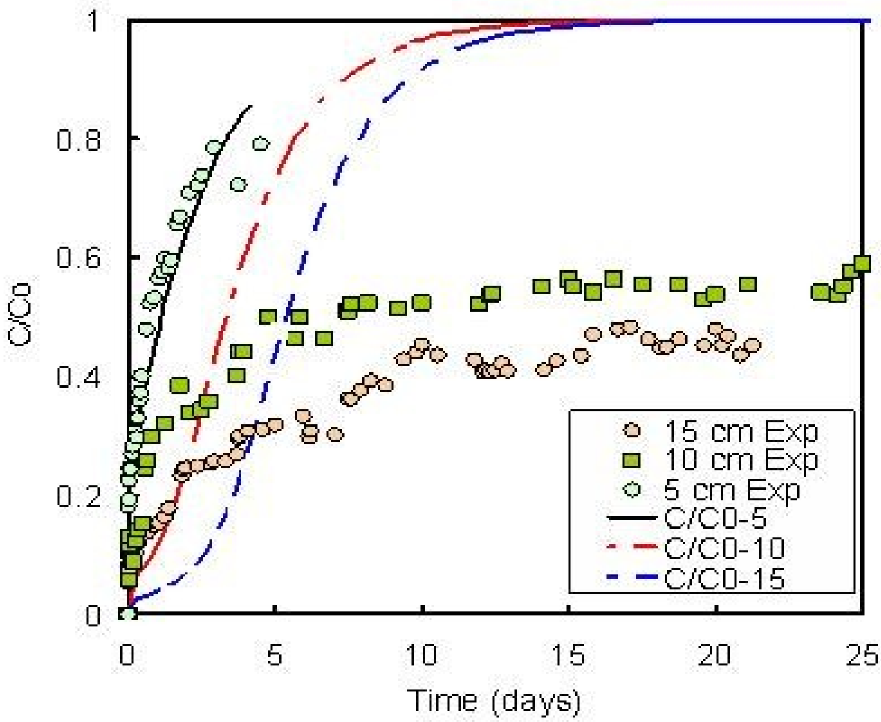

Figure 9. Variation of C/C_o of the GAC filter for various filter bed depths. Also shown is the fit between experimental data and model simulation for variation in bed depth. Filtration rate = 4 m/hr, average influent TOC = 10 mg/L. $k_f = 1.2e^{-5}$ and $k_s = 4e^{-8}$ for all modelling runs.

Figure 9. shows the fit with experimental data with different filter depths where the influent concentration and filtration rates held constant. Here the performance is expressed in terms of C/Co where C and Co are the concentrations of the effluent and influent respectively. The modelling parameters were kept constant for all modelling runs. The model is able to simulate the experimental results for bed depths of 5 cm. The modelling for the 10 and 15cm bed was less successful.

Figure 5. shows the fit with experimental data for the 5 cm bed depth where the filtration rates were varied. The simulated performance of the GAC filter shown in Figure 5 fitted reasonably well with the experimental data for velocities of 4 m/hr. The modelling for the 5 cm bed with a filtration velocity of 2 and 4 M/hr was less successful. It should be noted that this experiment uses the same data as one shown in Figure 4.

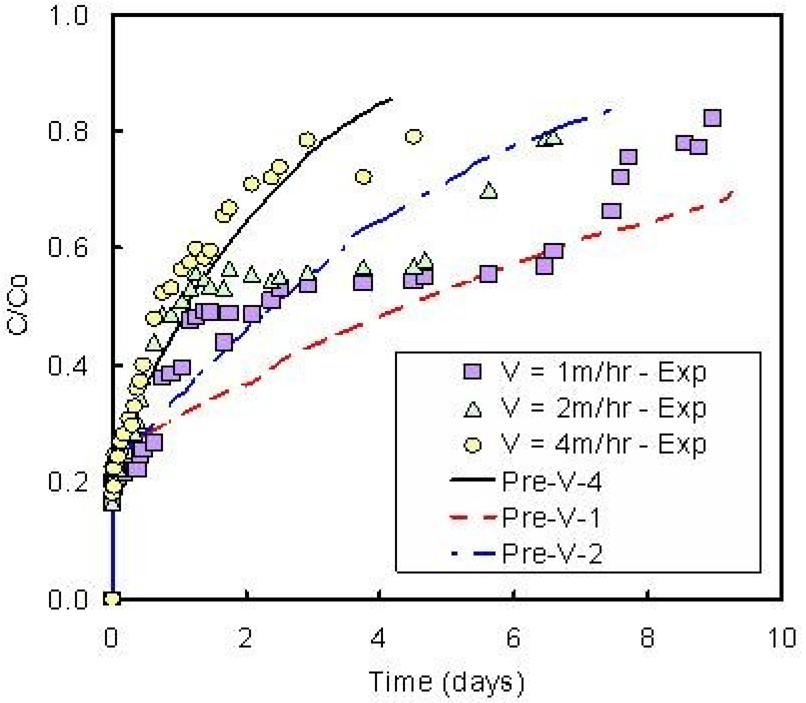

Figure 10 Variation of C/C_o of the GAC filter for various filtration rates. Also shown is the fit between experimental data and model simulation for variation in bed depth. Bed depth = 5 cm, average influent TOC = 10 mg/L.

The model simulation fits reasonably well during the initial period and also with a shallow bed depth (5 cm). This was also observed by Aneeta *et al.* (2000) [17] with fixed bed depth of less than 10 cm. The isotherm parameters used in this study were lower compared with previous research [17] because of the lower loading of metsulfuron methyl at 10 mg/L. This perhaps implies that the driving force for the GAC desorption of SOC (metsulfuron-methyl) decreases as the isotherm parameter decreases. With a larger GAC bed depth the exhaustion period therefore should be longer compared with smaller bed depths. In this study a GAC column of 5 cm bed depth exhausted after 6 days. The DOC of MM removed was 20% after 4 days of the comparable values of GAC bed depths of 50 % DOC removal (10 cm) and 67% DOC removal (15 cm) (Figure 3).

A near steady state occurs after 6 days with a bed depth of 10 and 15 cm. This phenomena may have resulted from the growth of some microorganism on GAC surface, especially in the exhausted portion of GAC [18] and may be attributed to partial biological growth and partial GAC adsorption. This is perhaps because at low concentrations of MM, the aerobic microbial activity is enhanced by the sufficient dissolve organic oxygen in the water ahead of GAC bed. More generally all GAC columns act as biofilters because GAC appear to remove any disinfectant in the top few centimeters of the bed. Some studies report that small values of the Freundlich isotherm slope present the possibility of small concentration gradients and significant irreversible adsorption to the GAC [11-12][19]. The driving force for desorption of GAC is critical because of the very short period of time available to transport the SOCs to the microorganism on the external GAC surface. Microbiology may also vary temporally and spatially within the GAC column. Depending on the point in its service life, a GAC column can contain three zones of varying length; exhausted GAC, partially exhausted GAC, and virgin GAC.

Unfortunately, very little work has been done on the biodegradation and non biodegradation of herbicides SOCs. Some research has shown that inoculate microorganisms can adsorb triazine and s - triazine in surface water [20]. Many nonbiodegradable SOCs may cause adverse health effects but this lack of research in the area of microorganism growth on GAC with sulfonyl urea herbicides is important and wants further research.

Batch Adsorption Doped Zn – TiO_2 GAC

The adsorption of C/C_0 doped Zn – TiO_2 GAC 0.025 %, 0.1%, and 0.125% are fluctuated comparing with GAC alone. So, in this experiment (Figure 5), doped Zn- TiO_2 GAC was not shown simulation with the model. These phenomena may occur from desorption of MM during the first period 20 min of adsorption [21]. The removal of MM in term of DOC was in the rang of 60 – 70 % while the highest removal of MM in term of DOC was 77% with the doped Zn- TiO_2 GAC 0.125% w/v.After that. MM was bring to put batch photocatalytic hybrid system.

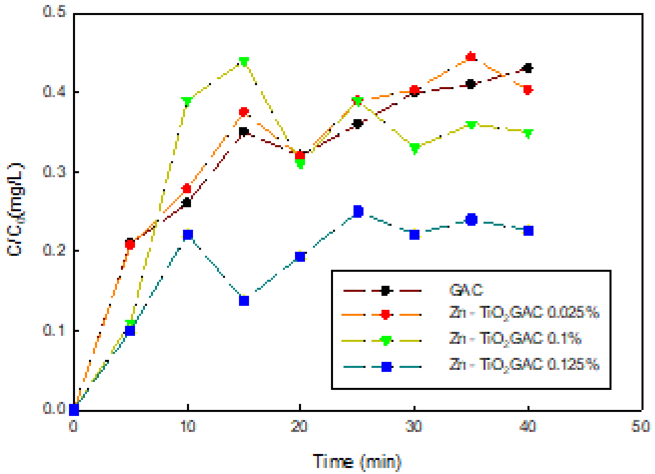

Figure 11 Variaton of C/C_0 GAC and doped Zn- TiO_2 GAC with 0.025%, 0.1% and 0.125% W/V (1mg/L, 120 rpm, 25 °C)

Batch Photocatalysis Hybrid System

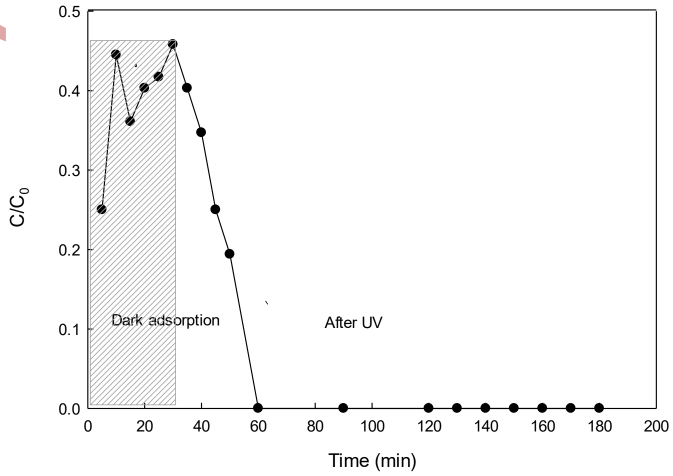

Figure 12 C/C_0 of MM solution after 0.125 %W/V adsorption couple with batch photocatalysis hybrid system UVC 254 nm 5 watts, 120 rpm, 25°C, covered with Aluminum foil.

Batch photocatalysis hybrid system was set up as shown in figure 6. The treated MM solution was put in batch photocatalysis system. In batch photocatalysis system, UV C light was turn off for 30 min. The doped Zn – TiO_2 GAC with 0.125% W/V 1 g/L was putted in batch system with 120 rpm, covered with aluminum foil. Temperature was controlled by tap water in water bath about 25°C. To observe dark adsorption process. The desorption of MM solution in termof dissolved organic carbon occured during the first period of 30 min without UV [22]. After turn on UVC, the photo catalytic oxidation can remove MM until zero within 30 min of operation.

CONCLUSIONS

The 10 and 15 cm deep GAC columns showed a steady state of effluent concentration. Modelling using GAC adsorption theory could not replicate the experimental results. This phenomenon is attributed to the formation of micro-organism (BAC) on the surface of GAC in addition to GAC adsorption. Freundlich and Sips isotherm parameters are relatively small. It means that with 10 and 15 cm GAC bed depths. The GAC in the column were not fully exhausted because the parameters of isotherm Freundlich and Sips models are small and the exhaustion time is extensive. The doped Zn – Tio_2 GAC batch experiments can remove MM in term of DOC from 60 to 77% by using different w/v of doped Zn onto TiO_2 – GAC. The highest remove of MM 77% by using batch experiment was 0.125% w/v Zn -TiO_2 GAC was hybrid with photocatalytic oxidation process by put UV C and same conditions with batch experiment covering with aluminium foil can eradicate the least of MM solution.

Future work; The fixed bed depth of GAC doping with Zn – TiO_2 should be done with different AOPs systems such as semi – batch and continuous systems. Finally, Membrane hybrid systems should be provided and coupling with fixed bed column and photocatalytic oxidation

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